Uniladorieu

CLASSIFICATION CANCELLED .

BY AUTHORITY OF

1.147

HARMIN A

TITLE

DATE

UNCLASSIFIED

m419=10792-101 NO4-06-01



DPSP-76-1007 RTR-1568

This document consists of 47 No. 43 of 44 Copies, Series A.

DISTRIBUTION

1-2.	H. W. Bellas	18. R. A. Scaggs	32., W. M. Olliff
3-5.	M. Bauer	19. J. A. Porter	33. H. R. Reeve
6.	W. R. Jacobsen	20. H. J. Groh, Jr.	34. H. T. Smoland
7.	E. L. Albenesius	21. R. F. Anderson	35. W. M. Taylor
8.	G. F. Merz	22. C. T. Axelberg	36. D. A. Ward
9.	L. W. Fox	23. D. R. Becker	37. H. E. Wingo
10.	J. L. Crandall	24. E. C. Bertsche	38. C. M. Patterson
11.	F. E. Driggers	25. P. A. Dahlen	39. E. C. Morris
12.	R. Maher	26. W. B. Daspit	40. R. C. Cooley
13.	J. M. Boswell	27. J. W. Little	41. G. H. Street
14.	W. J. Jacober	28. F. B. Longtin	42. Vital Records File
15.	W. P. Mason	29. S. Mirshak	(43) PRD Central File
16.	A. S. Barab	30. M. D. Moore	44. 706-C File
17.	D. E. Ward	31. J. H. Nuzum	
•			

January 14, 1976

TO: D. A. WARD

FROM:

F. B. LONGTIN F.B.L

CLASSIFICATION CANCELLED &

MODERATOR DETRITIATION BY CATALYTIC EXCHANGE

Classified by: F. B. Longtin Staff Chemist, Reactor Tech.

CG 753.1

This document was prepared in conjunction with work accomplished under Contract No. DE-DE-AC09-76SR00001with the U.S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161

phone: (800) 553-6847 fax: (703) 605-6900

email: orders@ntis.fedworld.gov

online ordering: http://www.ntis.gov/support/index.html

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062

phone: (865)576-8401 fax: (865)576-5728

email: reports@adonis.osti.gov

TABLE OF CONTENTS

<u>Page</u>
INTRODUCTION 4
SUMMARY · · · · · · · · · · · · · · · · · · ·
CONCLUSIONS
DISCUSSION
ERDA Tritium Management Studies
Proposed SRP Demonstration
SRP Reactor Tritium Characteristics
Tritium Reduction Factor
Separation Factor
Catalytic Liquid-Gas Exchange
Hydrophobic Catalyst
<u>Cost Studies</u>
Column Design 13 Costs 14 Net Gain 15
Program
Technical Uncertainty

TABLE OF CONTENTS

CONT'D

	Pag	<u>e</u>
Table I	Fundamental Reactor Parameters 20)
Table II	Dollar Benefit Data and Equations	L
Table III	Catalytic Exchange Facts 23	3
Table IV	Cost Data	į.
Table V	Coefficients of Net Gain Equation	5 .
Table VI	Cost Estimates for Selected Cases	5
Table VII	Uncertainties of Cost Study	7
Table VIII	Comparison of Possible Demonstration Plants 28	3
Figure 1	Definitions & Design Equations for Linear Detritiation Process	9
Figure 2	Time Response to Detritiation $(r* = 3) \dots 30$	О
Figure 3	Tritium Reduction Achieved at End of First Year 33	1
Figure 4	Comparison of Cumulative Benefit Functions 32	2
Figure 5	Separation Factors α for Isotopic Exchange in Liquid Water - Hydrogen Gas	3
Figure 6	Catalytic Exchange Detritiation for a Reactor 30	4
Figure 7	Column Design	5
Figure 8	Capital Costs for the Five Cases Defined in Table V	6
Figure 9	Typical Cost Analysis Results	
Figure 10	Years to Recover Capital Costs	8
Figure 11	Annual Net Gain After Long Operation	
Appendix A	Column Design Equations	0
Appendix B	Sources and Uncertainties of Design and Cost Data	2
•		
References		6

INTRODUCTION

Releases of tritium from the 100 Area constitute the largest and most obvious single source of off-plant radioactivity released (reference 1). Removal of tritium from reactor moderator offers one way to keep these releases as low as practical. E.R.D.A.'s division of Waste Management has a program to develop a catalytic exchange process for removing tritium from light and heavy water for which an in-house demonstration is desired (reference 2). We report here the results of a preliminary study to determine the practicality and potential benefits of conducting such a demonstration in connection with an S.R.P. 100 Area reactor. This report also serves to collect in one place the basic information needed in considering removal of tritium from reactor moderator by other methods (references 1, 3, 4).

SUMMARY

Reduction of moderator tritium will reduce 100 Area releases of tritium in the same proportion. It will also reduce the need and cost of basin deionizer regeneration in this proportion. There is a good chance that up to 75% reduction in moderator tritium can be achieved by catalytic exchange at an acceptable net cost (< \$20,000/year). There is even reasonable chance of recovering capital costs and ultimately achieving a net gain from reduced basin deionizer costs, for reductions in the range from 20% to 60%. Estimated costs and benefits for systems of different sizes, each for one reactor, are summarized as follows:

Ultimate tritium reduction factor Ultimate percent reduction Percent reduction in first year	1.6	2	6	20
	37.5	50	83.3	95
	4.6	7.7	33	75
Total capital costs, \$1000	82	110	350	1200
Annual operating costs, \$1000	35	43	120	390
Years to recover capital cost a		2.8	1.8	_b
Annual net gain after long operation a, \$1000		42	28	230
Reduction in off-site dose, man-rem/yr	11	15	25	28
Residual cost of off-site dose reduction, \$/man-rem	_c	_c	_c	8200 ^đ

^aCrediting all cost benefits except reduction in off-site exposure

b_{Never recovered}

No cost

d (Does not include \$20,000 unrecovered capital cost)

These are results of a crude cost analysis, which needs to be refined by combining results of bench testing now being started at Mound Laboratory with a detailed engineering design study, and a catalyst life test in a 100 Area.

A pilot plant using a one-inch I.D. catalyst-packed column and a feed rate of 0.7 gph would provide a satisfactory demonstration of the process feasibility from a technical and engineering viewpoint. It would cost very roughly \$60,000 in equipment and \$11,000 per year in operating costs, and could be incorporated easily as part of a full scale plant for permanent use. Results of the demonstration would be applicable directly to Candu type power reactors and by extrapolation to light water power reactors.

All cost estimates presented here are of a very preliminary nature, solely for the purpose of determining if further study of the catalytic exchange process is warranted.

CONCLUSIONS

- 1. The catalytic exchange process merits further study to firm up technical data, engineering design, and cost analysis results.
 - 2. This work should aim at
 - o a 100 Area test installation to determine catalyst life
 - o pilot plant demonstration using direct feed from a 100 Area reactor to an approximately 1" ID catalyst column
 - o full scale plant operation if the demonstration is successful.

DISCUSSION

E.R.D.A. Tritium Management Studies

E.R.D.A.'s division of Waste Management and Transportation is pursuing a program to develop methods of reducing releases originating from reactor water and wastes. Methods are needed because of the prospect that tritium in the coolant and moderator water of power reactors and in basin water of fuel reprocessing plants may soon reach levels such that consequent tritium releases will be of public concern. The approach being taken is that of removing tritium from the water and concentrating it to the point that it can be stored or buried safely and economically.

For the fuel basins and for U. S. power reactors, the tritium must be removed from light water (H_2O) . The Canadians have begun international sale of their Candu heavy water power reactors and there is some prospect of a number of these reactors in the U. S. in the near future (reference 5). In these reactors, tritium must be removed from D_2O .

The E.R.D.A. program includes investigation of a number of methods for removing tritium from $\rm H_2O$ and from $\rm D_2O$. Of these the one nearest to practical application is that of catalytic exchange of hydrogen isotopes between liquid water and hydrogen gas. Extensive work on this process has been done at the A.E.C.L.'s Chalk River Nuclear Laboratories (reference 6), for the separation of $\rm H_2O$ from $\rm D_2O$. E.R.D.A. sponsored bench-scale work on separation of tritium from $\rm H_2O$ and from $\rm D_2O$ has been started at the Mound Laboratory. To complement this work, an in-house pilot plant demonstration is desired probably in connection with an S.R.P. reactor.

<u>Proposed S.R.P. Demonstration</u>. Such a demonstration could be provided by using the process to remove tritium from the moderator of a 100 Area production reactor. It would serve the following purposes:

- o determine catalyst performance in contact with actual reactor moderator
- o verify the scale-up from bench to full scale operation
- o obtain more accurate data on the economics of the process

Results of the demonstration would be directly applicable to detritiation of Candu reactor D_2O . Because separation of tritium from D_2O is expected to be almost an order of magnitude more difficult than separation of tritium from H_2O , a successful demonstration would also virtually assure successful removal of tritium from light water.

Potential S.R.P. Benefits. Removal of tritium from the moderator of an S.R.P. 100 Area reactor could have the following benefits:

- o reduce 100 Area atmospheric and liquid releases of tritium in proportion to moderator tritium reduction
- o reduce basin purging in this same proportion, with a corresponding reduction in the liquid releases of radioactivity other than tritium
- o reduce the need for use of plastic suits <u>if</u> the tritium can be reduced by more than a factor of about 10 (reference 4a)
- o effect a cost saving from the value of recovered tritium.

Preliminary Evaluation. We have made a preliminary study to determine if the proposed process has enough chance of success to be worth pursuing further. To be successful it should produce a worthwhile reduction in moderator tritium and tritium releases at a reasonable cost. This is the criterion which is being applied to tritium control in power reactors and fuel reprocessing plants, and which is likely to be applied to S.R.P.

The heart of this study was therefore a cost-benefit analysis which is necessarily crude because certain essential data are not yet known with sufficient accuracy. A major objective of the analysis was to identify these unknowns as an aid to planning the development program.

The study showed that there is very good possibility that the catalytic exchange process can reduce moderator tritium by 50 to 75% at relatively minor net cost. There is even a fair chance that the process will more than pay for itself for tritium reductions of 20 to 60%.

In the following pages details of the study are presented in three major parts:

- o features which are characteristic of SRP reactors independent of the nature of the tritium removal process
- o characteristics of the catalytic exchange process
- o cost analysis of the overall process (which combines results of the preceeding two items)

in that order.

S.R.P. Tritium Characteristics

Pertinent characteristics of the SRP reactor system (with and without detritiation) are summarized in figure 1 and table I. At present the concentration of tritium in moderator, \mathbf{x}_t , has stabilized at a constant value, \mathbf{x}_0 . This stable tritium concentration is sustained by a balance between generation by the reaction D+n $\rightarrow T$ (rate = g), radioactive decay, (rate = V λ_t), losses (rate = Lx_t) and makeup (rate = Lx_m). This balance requires that \mathbf{x}_0 have the value given in the Definition block of figure 1, where Λ_0 has the value given in table I. The observed stable tritium concentration is in agreement with this calculated value.

The object of moderator detritiation is to reduce the moderator tritium concentration \mathbf{x}_t to some value lower than \mathbf{x}_0 . The heavily shaded block in figure 1, together with its three associated moderator streams labelled \mathbf{x}_t , $\mathbf{G}\mathbf{x}_0$ and $\mathbf{D}\mathbf{x}_0$ represent an unspecified tritium removal process for this purpose, not now installed. Its installation will alter the tritium balance to that shown by equation 1. Initially tritium is removed by losses plus detritiation at a rate $\mathbf{V}\mathbf{A}\mathbf{x}_t$ greater than the rate of generation plus makeup $(\mathbf{g} + \mathbf{L}\mathbf{x}_m)$ so that the amount $(\mathbf{V}\mathbf{x}_t)$ of tritium in the moderator must decrease at a rate $-\mathbf{V}\mathbf{d}\mathbf{x}_t/\mathbf{d}t$. Ultimately a new stable concentration \mathbf{x}_t * is reached so that \mathbf{x}_t no longer changes and $\mathbf{d}\mathbf{x}_t/\mathbf{d}t = \mathbf{0}$. Equation 1 then requires that \mathbf{x}_t have the value \mathbf{x}_t * given in the Definition block.

The approach of x_t to the ultimate stable value x_t^* follows equation 2, which is the solution of the differential equation 1. The time constant Λ of equation 2 has the value given by the Definition block. The quantity Λ_0 was the time constant for the period in which moderator tritium, starting from zero, approached the present stable value, following an equation analogous to equation 2.

Tritium Reduction Factor. We will express the extent to which moderator tritium is reduced either as per cent or by the tritium reduction factor r defined in the Definition block of figure 1. Thus a reduction factor r=10 represents reduction of tritium to one tenth its present value, x_0 . From this definition it follows that the percent reduction is $(1-1/r)\cdot 100\%$. Equation 2 can be rewritten in terms of r to become equation 3, which shows the course of tritium equally well whether expressed in terms of percent reduction or tritium reduction factor. Expressed in either way, the tritium reduction gradually approaches an ultimate limit, which is r* for the tritium reduction factor and $(1-1/r*)\cdot 100\%$ for percent reduction. At this limit, tritium is being removed as fast as it is being generated in the moderator.

Time Constant. The ultimate limit is approached faster the larger the time constant Λ . Equation 4 shows that this constant is proportional to the ultimate tritium reduction factor, r*. Thus the ultimate limit is approached sooner the larger the ultimate tritium reduction factor. This follows directly from the definitions of r, r*, Λ and Λ_O given in figure 1, which lead to equation 3. It results from the fact that a higher ultimate tritium reduction is achieved only by increasing the rate of tritium removal.

In several following sections we will consider the consequences of equations 2 through 4 and then return again to figure 1 to discuss equations 5 and 6.

Reactor Parameters. Equations 1 through 4 depend on the reactor parameters listed in table I. The listed values apply only to SRP 100 Area reactors. The $\rm D_2O$ loss rate L is an average value for the past several years; recent values are slightly lower. The listed value was chosen to be consistent with the present value of $\rm x_O$, which is the result of years of previous operation.

Typical Course of Tritium Reduction. The course of tritium reduction for a tritium removal process with ultimate reduction factor $r^* = 3$ is shown in figure 2. The percent of original tritium (equal to 100%/r) was calculated from equation 3. In this case only a 14 percent reduction is achieved in the first year. The ultimate 66.7% reduction is approached closely only after twelve years of tritium removal at the rate corresponding to $r^* = 3$. Figure 3 shows the tritium reduction achieved in the first year by tritium removal at other rates. High reduction can be achieved in the first year only by a process which has a high ultimate reduction factor r^* , requiring

a high removal rate and correspondingly high cost. This is a characteristic of the reactor system and independent of the type of tritium removal process used.

Figure 3 also shows the total amount of tritium recovered by the tritium removal process up to any time. Recovery is at the rate Dx_D , or DSx_t . The total amount recovered is obtained as $\int_0^t DSx_t dt$, with x_t expressed by equation 2.

Dollar Benefits. Of the benefits of moderator detritiation which we have enumerated for SRP reactors, three can produce dollar returns that can offset some or all of the cost of tritium removal. These are reduction in cost of regenerating basin deionizers, reduction in use of plastic suits, and recovery of the tritium. Because of the gradual way in which tritium concentration is reduced over a period of years, the annual dollar return from these sources changes with succeeding years of operation of the tritium removal plant. For this reason the economics of tritium removal can be better understood in terms of the total benefit (and total cost) accrued from the start of detritiation up to any specified time.

these three sources can be calculated for any tritium removal process. For each source of benefit, table II defines a unit benefit. For basin purging and plastic suit work it is the benefit per year from 100% reduction in moderator tritium (note that in this case of 100% reduction, only, the annual benefit is constant). For tritium recovery, it is the value of recovering all of the tritium now present in the reactor moderator. In each case the number of units of benefit accrued in t years of detritiation is expressed as a function of r* and t (see reference 7 for the mathematical derivation). These functions are illustrated in figure 4. Each equation in table II gives the cumulative dollar benefit as the product of this function times the dollar value of the unit benefit. In this way, if a better estimate of the dollar value of unit benefit becomes available, it may be substituted for the present value in the equation.

The equations in table II are used in the subsequent cost study to calculate the dollar returns from detritiation. The graphs in figure 4 give a qualitative picture of how each source of benefit contributes to the total dollar return. Of the three, only recovery of tritium provides an early dollar return; the higher the ultimate tritium reduction factor, r*, the sooner is this early return realized. Reduction of plastic suit work yields only negligible return for r* values less than 10, while most of the possible gain has been achieved at r* \sim 100, with little of any additional gain for r* > 100. The maximum possible gain from reduction of plastic suit work is too small to have much effect on the results of the cost analysis.

Table II also lists an equation for the cumulative reduction in off-plant exposure. A cumulative dollar value of reduction in off-plant exposure could be obtained from this equation by multiplying by a dollar value per man rem. We have not assigned such a dollar value, although reference 12 does give a value of \$1000 per man rem applicable to power reactors. Our approach instead, is to calculate the net cost as total cost less the dollar benefits from the other three sources. If this cost is reasonable and the tritium reduction is worthwhile, the detritiation process will be judged worthy of further study. This is in line with the policy of keeping activity releases as low as practical.

Separation Factor. The ability of a particular process to separate two substances is measured by its separation factor α . It measures the separation achieved in a single stage process in which the entering stream is separated into two product streams A and B which are at equilibrium; no greater separation can be achieved in any practical process. If x_A and x_B are mol fractions of one substance in these two respective streams, then $1-x_A$ and $1-x_B$ are the mol fractions of the other substance in the same two streams. The separation factor is defined as

$$\alpha = (\frac{x_A}{1-x_A})/(\frac{x_B}{1-x_B})$$

We will be considering for the most part very low tritium concentrations such that x_A and x_R are much less than unity. Then approximately

$$\alpha = x_A/x_B.$$

<u>Process Magnitude</u>. The size of equipment and cost of energy needed to effect a particular ultimate tritium reduction, r*, increase in proportion to the quantity of moderator which must be processed per unit time. The controlling quantity may be either of the two flow rates F or G of figure 1. Equation 5 of figure 1 can be used to calculate G; F is RxG.

The separation factor α for separation of tritium from D_2O is not large enough in any known process to give a large separation in a single stage. It is necessary to use a counter current process to achieve a large overall separation (measured by the ratio $S = x_D/x_t$). Examples of counter current processes are the 100 Area isotopic distillation columns in which two streams flow past each other in opposite directions to effect a separation. For such a process the factor (R-1)S appearing in equation 5 is expressed by equation 6. The processes in which we are interested can be designed economically so that m is small, while S is so large that S/(S-1) is practically unity. For such a process the reflux ratio R is close to unity. Consequently both F and G are approximately equal to $V\Lambda_O(r^*-1) \alpha/(\alpha-1)$. Process size and costs are thus proportional to $V\Lambda_O(r^*-1) \alpha/(\alpha-1)$.

The quantities V and Λ_0 are fixed parameters of the 100 Area reactors. Thus costs will be higher the higher the ultimate tritium reduction factor. For a specified value of r*, costs will be lower the higher the separation factor α , other factors being equal.

Applicability. Equations 1 through 5 and their consequences do not depend on the nature of the detritiation process as long as it is linear (as defined in figure 1). Thus, for example, table II and figures 2 through 4 apply to any linear detritiation process. All known countercurrent detritiation processes should be linear as long as the tritium concentration does not exceed about 1%. Even when the concentration does exceed 1%, deviations from the results presented in these tables and figures should be minor.

Equation 6 is restricted to countercurrent processes, but is otherwise equally general. Thus the expression $V\Lambda_O$ (r*-1) $\alpha/(\alpha-1)$ for the flow rates F and G is applicable to any countercurrent process as long as S is large and m is small compared to 1.

This concludes discussion of those features of tritium removal which are characteristic of S.R.P. reactors independent of the nature of the process.

Catalytic Liquid Gas Exchange. The process being studied at Mound Laboratory makes use of the reaction

$$DT + D_2O = D_2 + DTO$$

to separate tritium from D_2O . A special catalyst is used to make the reaction go at a useful rate at room temperature, where the exchange occurs between liquid D_2O and gaseous D_2 .

The corresponding exchange reactor between HD and D_2O has been used in large scale production of heavy water by the Norsk Hydro Company in Norway and by the Canadians at Trail, British Columbia (reference 8). The exchange between DT and D_2O is used in parts of the process for detritiation of D_2O in the reactor at Grenoble, France (reference 9). In these cases the catalyst used was effective only at higher temperatures in the absence of liquid water. The exchange between HT and H_2O has been proposed for detritiation of light water, and is being studied at Mound Laboratory.

One advantage of these exchange reactions is their relatively large separation factor, α , as compared, for example, to fractional distillation. Figure 5 shows the separation factors for exchange of hydrogen isotopes between liquid water and hydrogen gas vs temperature. At 22°C (72°F), the separation factors are 1.7 for the DT + H₂O exchange, 3.9 for HD + H₂O, and 7.1 for HT + H₂O. These relatively large α values mean that much smaller volumes of liquid and gas need to be handled than (for example) in fractional distillation of water for which α lies in the range 1.01 to 1.1.

The exchange reaction has one limitation. Because very strong chemical bonds must be broken, the reaction is normally very slow. To obtain any practical exchange of isotopes, a catalyst must be used to speed up the reaction. All of the catalysts available until recently for this purpose are deactivated by liquid water. It has therefore been necessary to first superheat the water before bringing it into contact with the catalyst. In a countercurrent process (needed to obtain any separation greater than that of a single equilibration), the gas must repeatedly be superheated to contact the catalyst and then cooled to contact a liquid stream in order to complete the transfer of isotopes. The process requires complex equipment and the repeated reheating is costly. In addition, the high temperatures needed to prevent formation of liquid water reduce the separation factor α (see figure 5), further increasing the costs.

Hydrophobic Catalyst. Recently, a hydrophobic ("water-proof") catalyst has been developed by the AECL Chalk River Laboratory (reference 6). It consists of platinum deposited on alumina pellets, with a coating of silicone or a suitable organic film.

With this catalyst, tritium could be removed from reactor moderator by the process diagramed in figure 6. The heart of the process is the column filled with catalyst pellets. Reactor moderator containing tritium flows down over the catalyst pellets, and out the bottom of the column. Part of the liquid D₂O leaving the bottom of the column is electrolyzed to produce deuterium gas (containing tritium) at one electrode and oxygen gas at the other. The rest of the D₂O is drawn off as a product stream. The deuterium gas is passed up through the catalyst column to undergo isotopic exchange with the down-flowing D₂O. Tritium is transferred from the gas to the liquid, so that the concentration of tritium in the ${\rm D}_2{\rm O}$ increases as it flows down through the column. The product stream drawn off from the bottom of the column is enriched in tritium as compared to the D₂O fed to the top of the column. The gas loses tritium as it rises through the column, so that the stream leaving the top of the column has a lower proportion of tritium to deuterium than the feed stream. At the top of the column, this D2 gas is recombined with the oxygen from the electrolytic cell to produce heavy water containing less tritium than that fed to the column from the reactor.

The Chalk River Laboratory has demonstrated this process on a laboratory scale for separation of H_2O from D_2O . Monsanto's Mound Laboratory has assembled equipment to test and demonstrate detritiation of both light and heavy water using this catalyst (reference 2).

<u>Process Characteristics</u>. A number of characteristics of the process were obtained in a visit to the Chalk River Laboratories (reference 2), which are important in assessing the practicality of this process for removing tritium

RTR-1568

from the 100 Area reactor moderator. These are listed in table III. Most important are those concerning catalyst life and H.E.T.P. (height equivalent to a theoretical plate). The catalyst will not last indefinitely because of radiation damage to the waterproofing film, and may need to be replaced once or twice a year. The H.E.T.P. is a measure of catalyst performance, which determine the height of catalyst column needed to effect a specified separation (reference 10).

On theoretical bases, a fixed volume of catalyst will be equivalent to one theoretical plate whether it is packed in a long narrow column or in a short fat column. For any particular separation process (e.g. the DT-D $_2$ O isotope exchange) the volume of catalyst per theoretical plate is a nearly constant multiple of the gas flow rate. This proportionality has been verified in the AECL tests over a range of liquid and gas flow rates. The proportionality constant falls off some only at the lowest rates tested. This constant is the catalyst volume constant listed in table III for the HD-H $_2$ O exchange, which we have estimated from other data in table III. We have used this same value for the DT-D $_2$ O exchange; theory (see Appendix A) indicates that this assumption may yield an overestimate of catalyst volume and costs.

Cost Studies

With the limited information now available, a cost study can determine if this process has enough promise to be worth further study. It can help identify areas where more information must be developed from laboratory and plant tests, and it can serve as a pattern for cost studies of alternative ways to remove tritium from the reactor moderator.

Column Design. Some of the process costs depend in an important way on the design of the catalytic exchange column and associated electrolytic equipment. For the present purpose the catalyst column was assumed to behave like an equivalent plate column. The methods used to design the column on this basis are sketched in Appendix A. The detailed calculations are documented in reference 7, p 10-28. The flow rates, catalyst volume, and column diameters obtained from these calculations are presented in figure 7. They are all of reasonable magnitude - a few inches diameter, a few cubic feet of catalyst, and a feed rate not more than 1 gpm. Note that the flow, catalyst volume, and column cross sectional area all increase with increasing tritium reduction in proportion to (r*-1).

In arriving at this design, an overall separation factor S=35 was used. A fairly large value of S is needed to reduce the volume of D_2O drawn off to a small value so that the cost of D_2O held in the process is not a major cost item. A value of S=35 will do this for tritium reductions not greater than about $r^*=6$. The design calculations show that eleven theoretical plates are needed to give S=35. For r^* greater than 6, more than 10 plates may

RTR-1568

be needed. This will increase the catalyst volume above that shown in figure 7, in proportion to S, if a column of uniform diameter is used. It is possible, however, to taper the column diameter in steps so that the total catalyst volume remains approximately that shown in figure 7.

A column with S=35 will not yield anything near pure T_20 or tritium in the drawoff stream. Further processing is needed to upgrade the product to this level. In principle it could be done in a single column of very many theoretical plates. If a column of uniform diameter were used, the catalyst cost could become prohibitive. This cost could be reduced by tapering the column, but with the practical limit of one inch diameter this cost reduction is not enough. The alternative, selected in this study, is to use the approximately 11 plate column ninety percent of the time to remove tritium from the reactor moderator and the remaining time to upgrade the product in a series of batch operations. The batch upgrading will be carried to the point that the tritium concentration is about 20%. At this point the 200 Area can accept it and complete the upgrading to essentially pure tritium (reference 11).

Costs. In the cost studies we have made no attempt to allow for inflation. All dollar values are in 1975 dollars. We assume that inflation will affect all costs in approximately the same proportion. If this is true, the effect of inflation is simply to multiply all of our cost and value figures by the same constant which converts from 1975 dollars to current dollars.

In table IV we have identified the important cost items and listed our best estimates of their magnitudes. The sources and uncertainties of the unit costs are discussed in Appendix B. Some are known accurately while some are at best only guesses.

Most of the listed unit costs are costs per gpy. The number of gpy needed to attain a given ultimate tritium reduction is $V\Lambda_{o}(r*-1)\alpha/\alpha-1=10,360(r*-1)$; values are listed (as feed rate, gpy)for r*=1.6, 2 and 6. The actual cost for each item is the product of unit cost times this feed rate; these actual costs are tabulated for r*=1.6, 2 and 6. These r* values represent, respectively, the smallest practical column diameter and the probable lower and upper limits of column size likely to be used for a full scale plant.

Items 1, 5 and 12 are calculated differently. Item 1, the actual electrolytic cell cost is \$83 multiplied by the six tenths power of the feed rate. Items 5 and 12 are flat charges independent of the feed rate, hence independent of r*.

The total capital cost and total annual cost are obtained by summing the individual values. This leads to the equations from which they can be calculated, given at the bottom of the table. For the cost study we will use the cumulative cost, which is (capital cost) + (annual cost x years operation). Figure 8 shows how the cumulative net cost depends on r* for the several cases defined in table V.

RTR-1568

Net Gain. The net gain accrued from the start of detritiation up to anytime t (or cumulative net gain) is the cumulative dollar benefit less the cumulative cost for that period. If negative it represents a net cost. It is calculated by combining the results in tables II and IV, in the form of the equation given in table V.

Figure 9 presents the results of this calculation for selected values of the ultimate tritium reduction, r^* . For $r^* = 1.6$, 2 and 6 the costs and benefits break even after a few years operation and beyond that point the tritium reduction is obtained and maintained at no net cost. Instead there is an actual net gain at an annual rate which eventually becomes constant. On the other hand, for a value of r^* large enough to effect significant reduction in plastic suitwork ($r^* = 20$), the initial cost is high (\$1.15 million/reactor) and after 4 years operation additional costs accrue annually at a \$0.22 million/reactor year.

Three features of these cost histories are of particular interest: - the initial or capital cost at time t=0, the time required to recover the initial cost (the "break-even point" at which the curve crosses the line of zero net gain), and the annual net gain or loss (slope of the curve) after the curve straightens out. These three features alone give a rough feel for the whole cost history. Note that the curve for $r^* = 20$ in figure 8 has no break-even point; this can be true for other cases and other values of r^* .

Figure 9 presents only our present best estimate of net costs or gains, corresponding to case I of table V, and only for selected values of the tritium reduction factor r*. The way the economics of tritium removal changes with r* and with changes in the basic cost estimates is summarized in figures 8, 10 and 11, which show the initial cost, years to recover initial cost, and annual net gain after 10 to 20 years of detritiation, respectively.

Figure 8 has already been discussed. Figure 10 shows that the time required to recover the initial cost is short only for the two most favorable cases (Cases I and II of table V), and then only for r* values greater than about 2. In every case the time to break even is very long for values of r* approaching one, and for values of r* approaching an upper limit value which is different for each case. Any process designed to produce an ultimate tritium reduction factor greater than this upper limit will never recover the initial cost.

Figure 11 shows the average annual net gain (or cost, if negative) over the period from t=10 to t=20 years. Beyond about ten years of detritiation the annual costs change rather little with passage of time, so that the annual costs shown in figure 11 can be considered as roughly representative of any year after the detritiation process has been in operation for ten years or more.

A hypothetical cost limit curve is shown in figure 11. It stands in place of actual data, not now available, on the greatest annual net cost that might be accepted in order to achieve any desired reduction in off-plant tritium

releases as expressed by r* (or the corresponding percent reductions shown by the scale at the top of the graph). This curve is given only to make the following discussion concrete. The actual limit curve may be quite different.

If the cost limit curve of figure 11 were to be accepted, the figure shows that the annual net cost (negative values of annual net gain) becomes unacceptable only for tritium reductions greater than a limit that ranges from 4.5 for case IV to 13.9 for case II. Regardless of what the cost limit may be, for the cases listed in table V there is a range of r* values within which reduction of moderator tritium and associated off-plant tritium exposure can be achieved at no net cost. For case IV it is the range from r* \sim 1.1 to r* = 3.7, while for case II it is the range from r* \sim 1.05 to r* = 11.2. For r* values near the middle of this range, figure 11 shows actually a substantial net dollar gain from the detritiation process. For any time beyond the break-even point of figure 10, this annual net gain is clear of any unrecovered costs.

These results of the cost study indicate that the catalytic liquid-gas exchange process offers a very good prospect of providing 20 to 75 percent ultimate reduction in tritium releases ($r^* = 1.6$ to 4) at acceptable cost or even no net cost in the long run. There is even some chance of reductions as high as 92 percent at acceptable cost. But significant elimination of plastic suit work would be too costly unless it were justified by a high incentive to reduce off-plant tritium releases by more than the 95% ($r^* > 20$) which it would require.

Program

The cost study indicates that further work toward developing a catalytic exchange process for removing tritium from reactor moderator is warranted. This work falls into three phases:

- o work to eliminate the technical uncertainties which are apparent in the present study
- o a pilot plant test to demonstrate practicality of the process and help in selecting the best design for a full scale plant
- o design and installation of the full scale plant if the pilot plant demonstration is successful.

Technical Uncertainties. The uncertainties in the data used in the cost study are presented in detail in Appendix B. In general they stem from either technical uncertainties as to the performance of the catalytic exchange process or from the very preliminary and superficial nature of the process design study used to obtain only rough cost estimates. Much of this uncertainty can be removed by bench scale test work such as that being done at Mound Laboratory together with a more detailed engineering design study.

-3.7

Table VII summarizes the uncertainties listed in Appendix B and ranks them in importance, in proportion to their effect on the net cost (or net gain) of detritiation. The most important are those in graph A of table VII; together they account for about 80 percent of the uncertainty in the cost analysis.

Most important is the uncertainty in catalyst life and theoretical plate height. The Mound Laboratory tests will establish the plate height, and also the electrolytic cell power requirement. A 100 Area test is needed to establish the catalyst life. A more accurate estimate of the cost of basin purging can be obtained by a more detailed analysis of 100 and 200 Area costs of deionizer regeneration. The remaining three items in group A require detailed engineering design studies of the processes of tritium removal and upgrading. These studies will also reduce most of the uncertainties listed in groups B and C.

Catalyst Life Test. Catalyst life depends on the impurities present in the water being tested. Non-radioactive impurities cause catalyst poisoning. It is possible to regenerate the catalyst, but it might not be economic to do so. Radioactive impurities could cause radiation damage to the waterproofing film on the catalyst pellets. The material of the film which has given the best performance to date is one of those most susceptible to radiation damage. Others are available which are less susceptible to radiation damage but which give poorer performance. A catalyst which has suffered radiation damage could not easily be regenerated, although the value of the platinum could be recovered.

A test of catalyst life is needed to determine if the more radiation resistant waterproofing is needed and to provide a better estimate of catalyst life for use in refined cost studies. It would also determine if catalyst regeneration is feasible and by what method, so that provisions for catalyst regeneration may be included in the final process design if needed.

This test will give reliable results only if the water to which the catalyst is exposed has exactly the same impurity content (especially radio-active) as the final detritiation plant must process. Short lived radionuclides will probably be the major source of radiation damage. Their effort cannot be reliably duplicated by either a synthetic feed stream or by a feed of water removed from the 100 Area reactor and carried elsewhere to do the testing. Thus the test must be done on a moderator stream fed directly from the reactor system into the test catalyst column.

Conceptually, the test might be done in a one inch diameter catalyst column three feet in height operated at total reflux (i.e., no drawoff). The equipment required would consist of items 1, 2, 3 and 8 of table IV. Costs for items 1 and 2 would be those listed under $r^* = 1.6$ in table IV. Costs for items 3 and 4 would be about five percent of the listed values because of the much shorter catalyst column (about .03 times the length of the 11 plate column). Thus the equipment cost for the test would be about \$26,000. With forethought in design of the test setup, the electrolytic cells and electrical auxiliaries could be used for the pilot plant after the catalyst life test is completed.

Pilot Plant Demonstration. A fully satisfying demonstration would accomplish the following:

- 1. Confirm on a plant scale the technical data obtained from laboratory tests
- 2. Confirm the engineering design
- 3. Provide a firm cost analysis
- 4. Show a substantial tritium reduction in a reasonable length of time and at a reasonable cost

The first three items can be demonstrated with a plant using a one inch I.D. catalyst column to give an ultimate tritium reduction of 38 percent; this is the smallest and least expensive practical plant. But for a plant of this size the approach to the ultimate reduction is so slow that it cannot be used to demonstrate the fourth item. Only a much larger and more expensive plant can do this.

From the standpoint of item 4, the demonstration plant should be one which gives at least a 30% reduction of moderator tritium, and at least half of its ultimate reduction in a demonstration period of one to three years. Table VIII summarizes the estimated costs and tritium reduction performance of catalytic exchange detritiation plants of three selected sizes. A plant of size $r^* = 1.6$ obviously does not meet the requirements of item 4. The desired size lies in the range $r^* = 3$ to 6. The most satisfying results would be obtained with the largest sized plant, but the costs become large.

A conservative approach is to do the demonstration in two stages. First operate a small plant (r* = 1.6) to firm up the cost analysis, and then expand the plant to the largest practical size to complete the demonstration. The plant size can be expanded easily by adding catalyst column sections of larger diameter at the feed end. Addition of a three plate section of twice the cross sectional area will double (r*-1). Each added section must be provided with electrolytic cells capable of electrolyzing D_2O at a rate equal to the increase in feed rate occasional by the increase in plant size. This results in a column tapered in cross section at close to the optimum size (reference 7, p 10-27).

Initially the tritium product from the small (r* = 1.6) plant would be upgraded only to the point that it could be stored economically. Purchase of equipment needed in the 200 Area to complete upgrading would be deferred until it was certain that detritiation of 100 Area moderator would become a permanent operation. The costs listed in table VIII pertain to operation without 200 Area upgrading.

While a plant of size r*=1.6 produces no dramatic reduction in moderator tritium in the first year, its performance can be checked reliably in a number of ways. Cost data are obtained easily during fabrication and operation. The achieved reduction in moderator tritium will be only 4.5% in the first year, but this is large enough compared to the uncertainties of measurement to give a reliable check on the predicted reduction. Furthermore it can be checked by material balance methods from the amount of tritium collected in the drawoff stream. The column performance and H.E.T.P. can be checked by the observed ratio $S = x_D/x_t$ of tritium concentration in drawoff to feed streams. The column throughput capacity can be checked by observing the feed rate and electrolysis rate that the column can handle without deterioration in the ratio S. Operation of this plant will also give experience with operating characteristics, which will be valuable in designing a full scale plant.

Full Scale Plant. If experience with the pilot plant shows that the process is practical for plant use, installation of a full scale plant in each reactor area should then be considered. The full scale demonstration plant would serve as a prototype for the plants to be installed in the other reactor areas. They should be designed to facilitate further expansion by adding on column sections, should the need arise.

FBL/1bw

SECRET

- 20 -

DPSP 76-1007

RTR-1568

Table I

FUNDAMENTAL REACTOR PARAMETERS

1. Moderator Volume

V = 52,500 gallons

2. Moderator Loss Rate

L = 1000 lb/mo = 1299 gallons/year (gpy)

3. Tritium Decay Constant

 $\lambda = .0565/yr$

4. Time Constant for Tritium Transients

 $\Lambda_{o} = \lambda + L/V = 0.0813/yr$

5. Detritiation Feed Rate Coefficient

 $V\Lambda_{o} = 4267 \text{ gpy}$ = 0.4871 gallons/hour (gph) = 0.008128 gpm

The sources and accuracy of these data are discussed in Appendix B.

DPSP 76-1007

SECRET

RTR-1568

Table II

DOLLAR BENEFIT DATA AND EQUATIONS

(Basis: Single Reactor)

A. Release to Environment

1. Off-plant exposure from 100 Area tritium

29.8 man rem/reactor year

2. Cumulative reduction in exposure

29.8(1-1/r*) [t-(1- $e^{-\Lambda t}$.)/ Λ] man rem

3. Dollar value of unit reduction:

none claimed (but see reference 12)

B. Basin Purging

 No. of deionizer regenerations for purging

70/reactor year

2. Cost per regeneration

\$1300

3. Benefit from 100% reduction

Cumulative benefit + =

\$91,000/year

\$91,000(1-1/r*)[$t-(1-e^{-\Lambda t})/\Lambda$]

C. Plastic Suit Work

1. No. of plastic suits used

1,300/reactor year

Plastic suit cost plus cost of extended working time

\$12.20/suit

3. Benefit from 100% reduction

\$16,000/year

Cumulative benefit =

\$16,000 (a + bt)

Range	Value of a	Value of b
r* ≤ 5	0	0
5 < r* < 286	-1/r*(1-5/r*)[49-34.034(1-r*/130) ²]	(1nr*/5)/1n20
r* ≥ 284	0	1

t = time in years

DPSP 76-1007

D. A. WARD

<u>SECRET</u> - 22 -

RTR-1568

Table II
(Cont'd)

D. Value of Tritium

1. Total amount in moderator

410 gm/reactor

2. Unit value

\$2440/gm

3. Total value

\$1,000,000

Cumulative benefit + \$1,000,000(1-1/r*)[$\Lambda_0 t + (1-1/r*)(1-e^{-\Lambda t})$]

The sources and accuracy of these data are discussed in Appendix B. The derivation of the equations is given in reference 7, p 2, 3, 29-39.

t = time in years

SECRET

RTR-1568

Table III

CATALYTIC EXCHANGE FACTS

(Information obtained from visit to Chalk River Laboratories; reference 2)

1. Catalyst Characteristics

- o dimensions 1/4" to 1" pellets. Column diameter should be about 6 x pellet dimension (: minimum column diameter \sim 1")
- o catalyst life limited by poisoning, waterlogging, radiation damage.
 - poisoned by plating out of noble metals; 100 Area impurity level too low to do this
 - waterlogged catalyst can be restored by heating
 - poisoned catalyst can be regenerated chemically
 - radiation damage to the waterproofing film could be permanent
- o volume requirement

(Column cross sectional area) (H.E.T.P.) */(Flow rate) = catalyst volume constant

2. Laboratory Column Characteristics (H₂O-D₂O system)

Diameter = 1 in.

Height = 3 ft.

Liquid flow rate = 50 cc/min = 0.8 gph

H.E.T.P.* \cong 10 ft.

Column cross sectional area = 0.0796 in^2

Catalyst volume constant = .068 cu ft/gph/plate

= 7.8×10^{-6} cu ft/gpy/plate

separation. It varies with flow rate in such a way that the catalyst volume constant remains nearly constant over the whole range of flow rates in which the liquid is well distributed over the packing and the column is not flooded.

^{*}H.E.T.P. is the height of catalytic bed which will perform like a single "theoretical plate" as defined in Appendix A.

It determines the height of column needed to effect a specified degree of

Table IV

COST DATA

(Basis: one reactor)

	Unit*	Costs Fo	r Selected C	ases**
	Cost	r* = 1.6	r* = 2	r* = 6
Column diam. (inches) Feed rate [(gph)	tion	.94 .709 6211 37.5	1.22 1.18 10,363 50	2.72 5.91 51,770 83.3
າ	CAPITAL COSTS			
1. Electrolytic Cells	*83'(gpy) ^{0.6}	\$16,000	21,000	56,000
2. Electrical auxiliaries	*1. 60/gpy	10,000	17,000	83,000
3. Column hardware	\$2.00/gpy	12,000	21,000	103,000
4. D ₂ O Inventory	\$0.45/gpy	3,000	5,000	23,000
5. 200 Area tritium process	\$35,000	35,000	35,000	35,000
6. Other capital costs	\$1,00/gpy	6,000	10,000	52,000
TOTAL CAPITAL COSTS	+ ,	82,000	109,000	352,000
	ANNUAL COSTS			
7. Electricity	\$0.46/gpy	\$ 2,900	4,800	24,000
8. Catalyst	\$0.32/gpy	2,000	3,300	17,000
9. Cooling water	\$0.0011/gpy		negligible	
10. Labor	\$0.087/gpy	500	900	5,000
11. Maintenance	\$0.28/gpy	1,700	2,900	14,000
12. 200 Area tritium process	\$24,000	24,000	24,000	24,000
13. Other annual costs	\$0.70/gpy	4,400	7,300	36,000
TOTAL ANNUAL COSTS	+	35,500	43,200	120,000

^{*}Sources and accuracy of these costs are discussed in Appendix B. Items 1, 5 and 12 are total costs rather than unit costs.

^{**}For (gpy) we use the feed rate $V\Lambda_0(r*-1)\alpha/\alpha-1$) = 010,363(r*-1) +Total capital cost = \$5,05 · (gpy) + \$83 · (gpy) + \$35,000 = .0523(r*-1) + .0213(r*-1) $^{0.6}$ + .035 \$million

Total annual cost = $$1.848 \cdot (gpy) + $24,000$

^{= .0192(}r*-1) + .024\$million/yr

SECRET

RTR-1568

Table V

COEFFICIENTS OF NET GAIN EQUATION

(Basis: one reactor)

CASE		<u>a</u>	b	С	р	a
						
I. Standard case (based on I-IV data)	tables	.09	1	.0213	.0523	.0192
I. Best case (Appendix B extreme val factors selected to gi largest net gain)		.11	1.12	.0114	.0267	.0192
I. Worst case (Appendix B extreme val to give smallest net g		.08	.88	.0312	.0779	.0228
V. Case I with costs doubl	ed	.09	1	.0426	.1046	.0384
V. Case I without tritium	value	.09	0	.0213	.0523	.0192

Cumulative net gain (\$million) =
$$a(1-1/r^*)[t - (1-e^{-\Lambda t})/\Lambda] \qquad \text{(basin deionizer savings)}$$

$$+b(1-1/r^*)[\Lambda_0 t + (1-1/r^*)(1-e^{-\Lambda t})] \qquad \text{(tritium value}$$

$$-[(p+qt)(r^*-1) + c (r^*-1)^{0.6}] \qquad \text{(100 Area cost)}$$

$$-(.035 + .024t) \qquad \text{(200 Area cost if tritium is recovered; omit in Case V)}$$

Table VI

COST ESTIMATES FOR SELECTED CASES

(Basis: one reactor)

Ultimate Tritium Reduction Factor, r*	1.6	· 2	√ 6	20
Ultimate Percent Reduction	37.5	50	83.3	95
Actual Reduction in First Year (%)	4.6	7.7	33	75
Capital Cost, \$million				
Standard Case	.082	.11	.35	1.2
Range	.059 to	.073 to	.106 to	.61 to 2.3
Years to recover capital cost				
Standard Case	4.8	2.8	1.8	- *
Range	$\begin{bmatrix} 2.4 & to \\ 12 \end{bmatrix}$	1.4 to 8.7	.63 to _*	_* _*
Annual net gain after long operation, \$thousand**				
Standard Case	26	42	23	-230
Range	$[\frac{39}{15} $ to	60 to 23	66 to -76	-590 to -130

First value is Case II, second value is Case IV of Table V

^{*}Capital cost not recovered at any time (as illustrated by the curve for r* = 20 in figure 6)

^{**}Negative values represent an actual net cost (rather than gain)

Table VII
UNCERTAINTIES OF COST STUDY

Group*	Cost Benefit Item	Nature of Uncertainty	Importance Rating
Α.	Catalyst	Plate height, catalyst life	39
• •	Tritium value recovery	Overall feasibility	18
	Other annual costs	Nature and value	14
	Basin purging	Exact value	9 .
	Column hardware	Nature and cost	6
. В.	Electricity	Cell power requirement	4
	Electrical auxiliaries	Detailed requirements	4
	Other capital costs	Nature and cost	5
	Maintenance	Amount required	3
	Labor (as operating cost)	Amount required	3
	Electrolytic cells	Exact cost	2
С.	Plastic suit work	Exact value of benefit	< 2
,	D ₂ O inventory	Process design	1
	Cooling water	Exact cost	0

^{*}Group A is of major importance, group B minor and group C of negligible importance in influencing the calculated net gain or cost.

The rating is in proportion to the effect of the uncertainty on calculated net gain; it is only relative and semi-quantitative. Estimated as the product of the uncertainty times the total contribution of the item to cost or benefit.

Table VIII

COMPARISON OF POSSIBLE DEMONSTRATION PLANTS

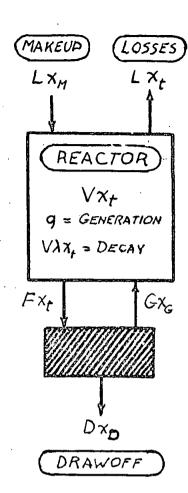
			<u>.</u>	Ad	chieve	d Triti:	ım Redi	uction+	
Size (r*)	Costs (\$TI	nousand)** Annual	Ultimate x % Reduction	25% Ultir <u>Y</u>	of	50% Ultin Y	of	75% Ultim Y	
1.6	47	11	38	2.2	9	5.3	19	11	28
3	140	38	67	1.2	17	2.8	33	5.7	50
6	320	96	83	0.6	21	1.4	42	2.8	62

^{**200} Area Costs not included

 $^{^+}$ Y = years to achieve indicated reduction

P = (1-1/r) · 100 = actual percent reduction in tritium concentration Ultimate % reduction = (1-1/r*) · 100

[%] of Ultimate reduction = $(actual/ultimate) \cdot 100$ = $100 \cdot (1-1/r)/(1-1/r*)$



Design Equations

- 1. $V dx_t/dt = 9 + Lx_H V \wedge x_t$
- 2. $\chi_t \chi_t^* = (\chi_o \chi_t^*) e^{-\Lambda t}$
- 3. $(1-1/r) = (1-1/r*)(1-e^{-\Lambda t})$
- 5. G = VA. (x-1)/(R-1)5
- 6. $(R-1)S = \left(\frac{\alpha-1}{\alpha}\right)(1-m)S/(S-1)$ $\cong (\alpha-1)/\alpha$

tvalid only for countercurrent processes

Definitions

XD, XG, XM, Xt: Tritium concentrations

D,G, F, L : D,O flow rates

V: DO VOLUME

9 : tritium generation rate

m : design parameter 0<m<1

a: tritium separation factor

S=XD/Xt = constant for Linear process

VNo = VA +L

V1 = V10 + DS

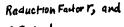
 $\chi_t^* = (g + L \chi_H) / V \Lambda$

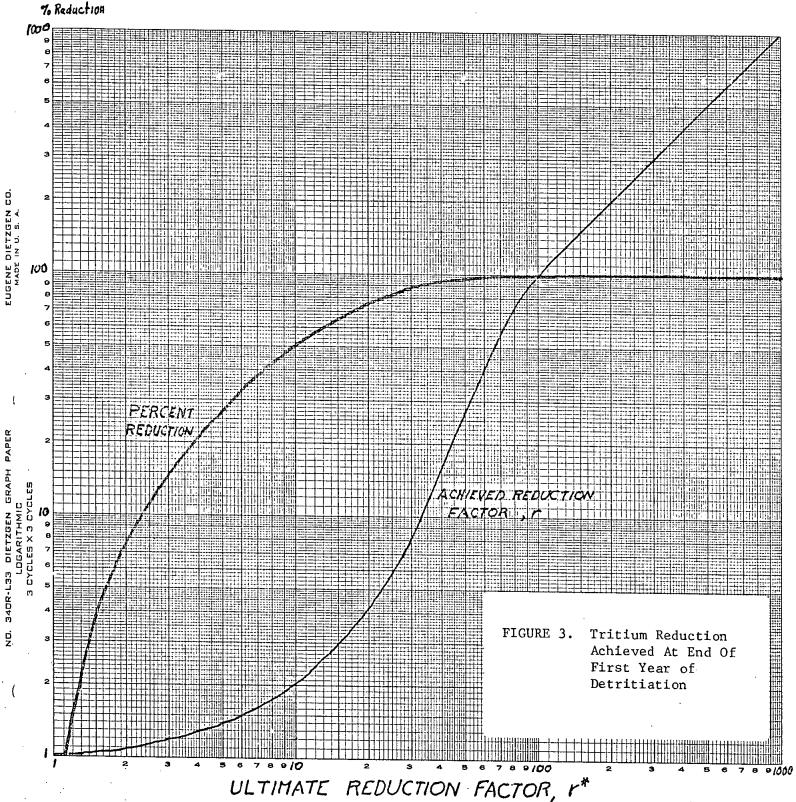
 $\chi_a = (g + L \chi_n) / V \Lambda_0$

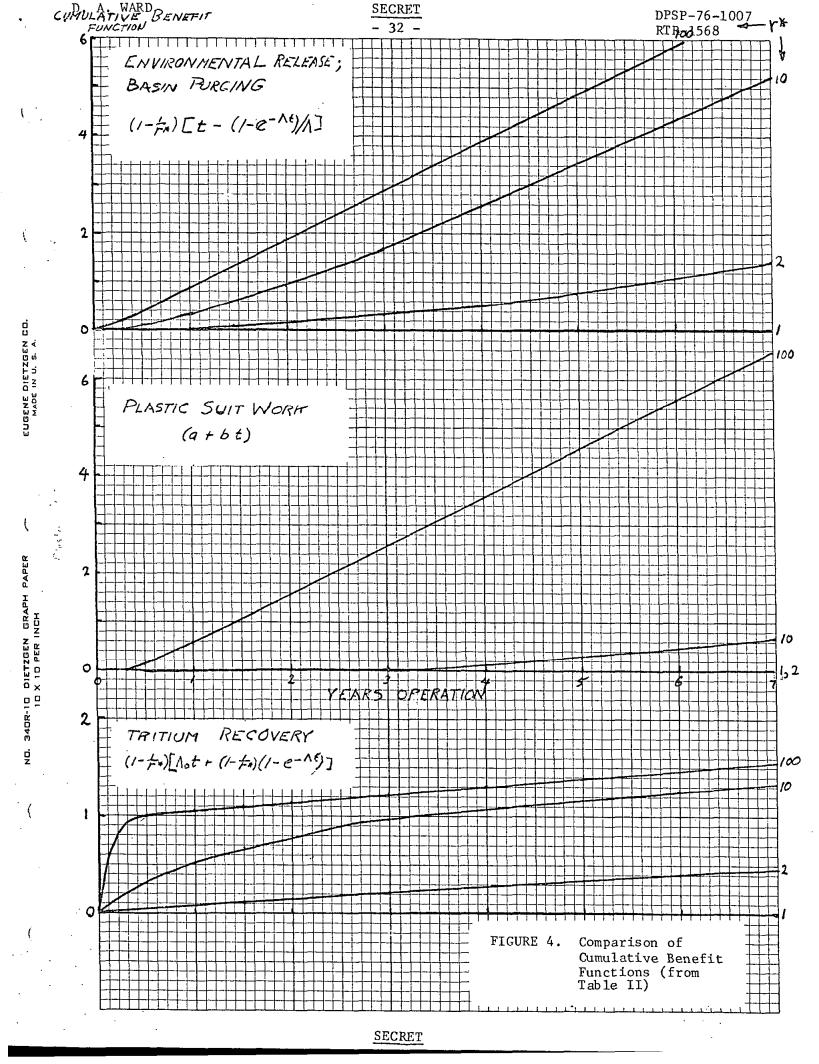
 $h = \chi_o/\chi_t$ $h^* = \chi_o/\chi_t^*$

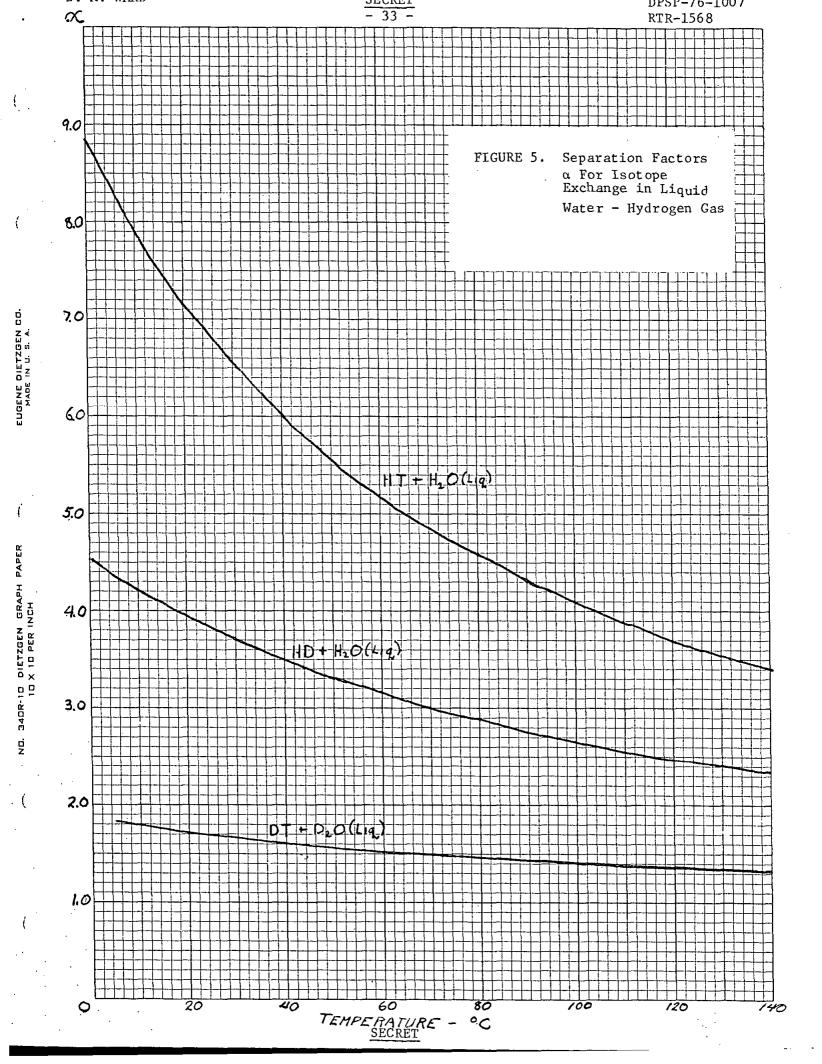
R = F/G
*Denotes ultimate steady state value of variable

FIGURE 1. Definitions and Design Equations for a Linear Detritiation Process EUGENE DIETZGEN CO. MADE IN U. S. A.









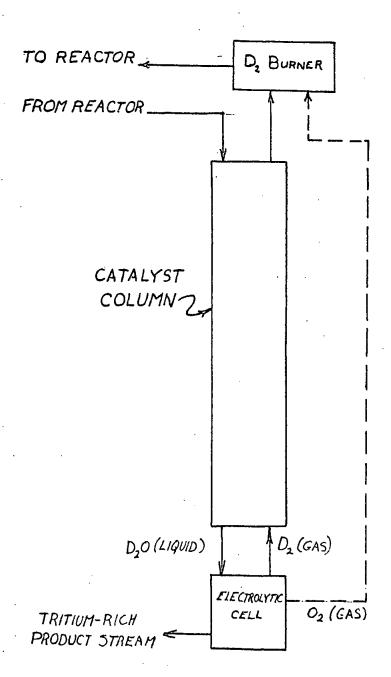
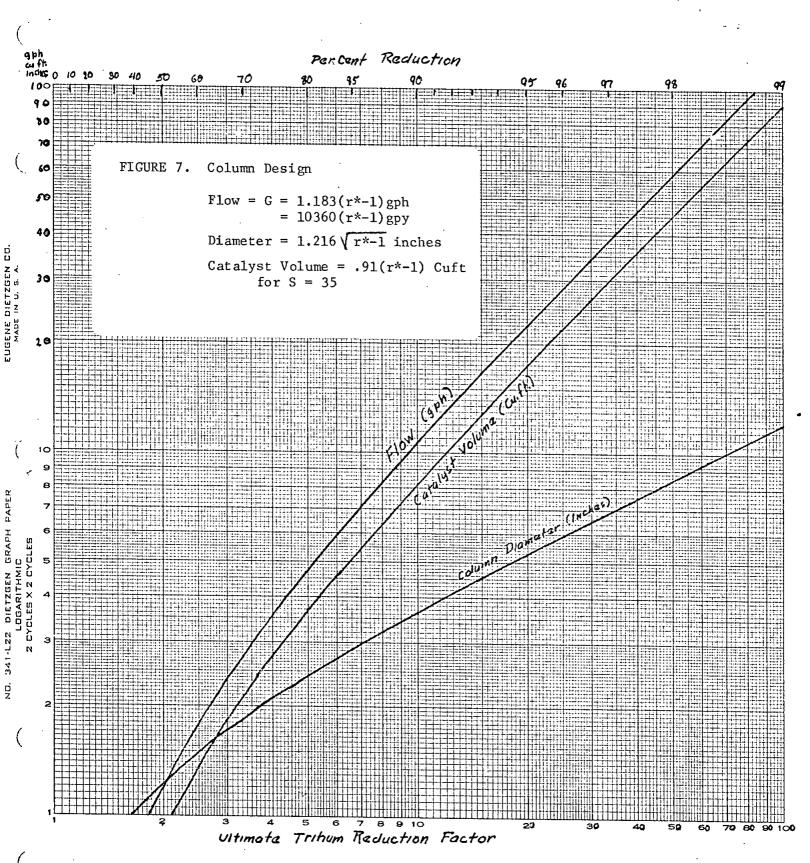
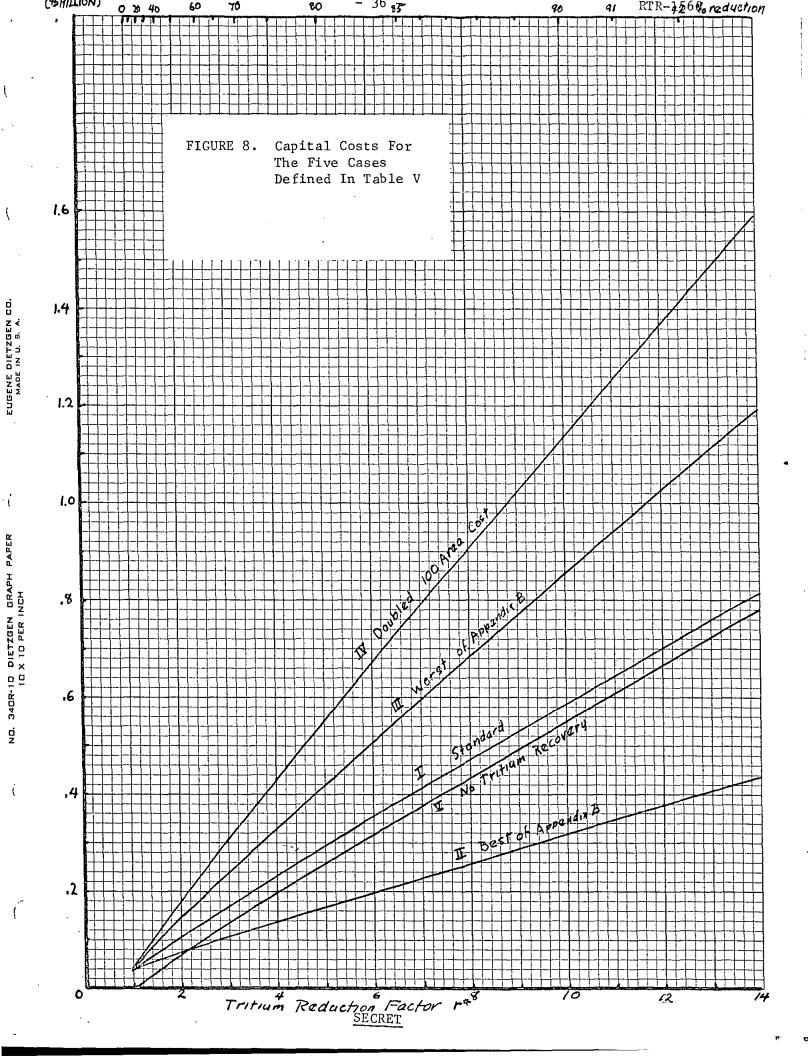
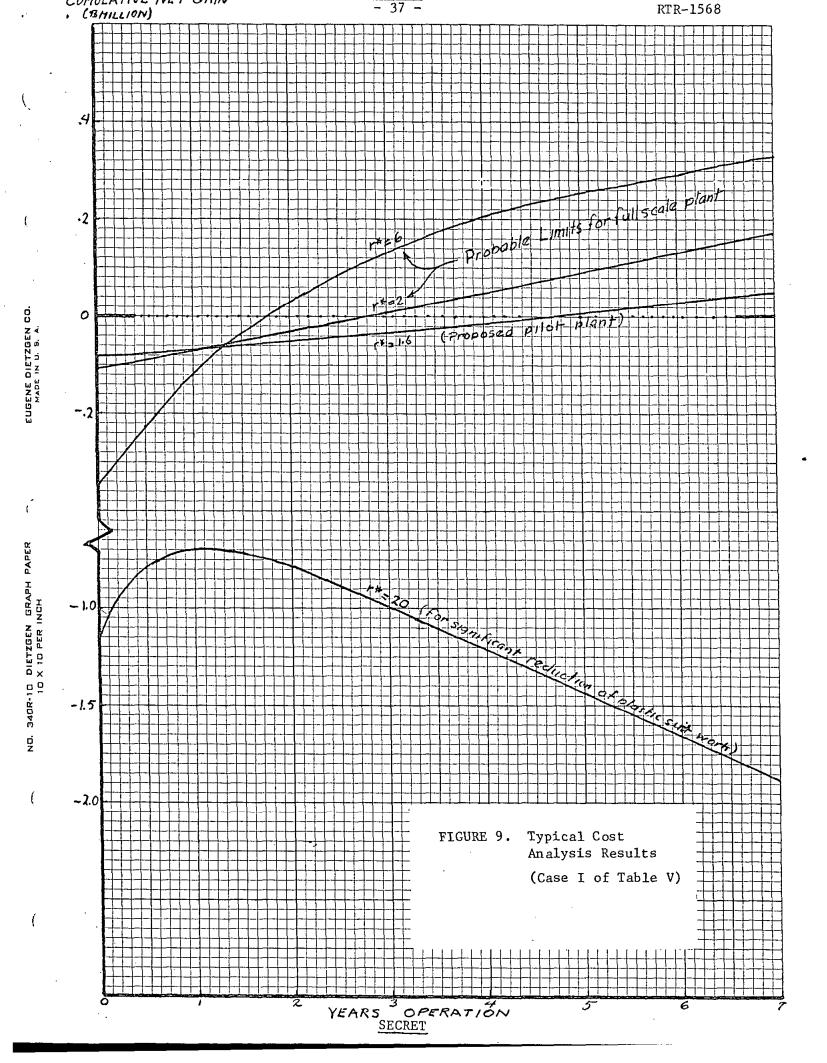
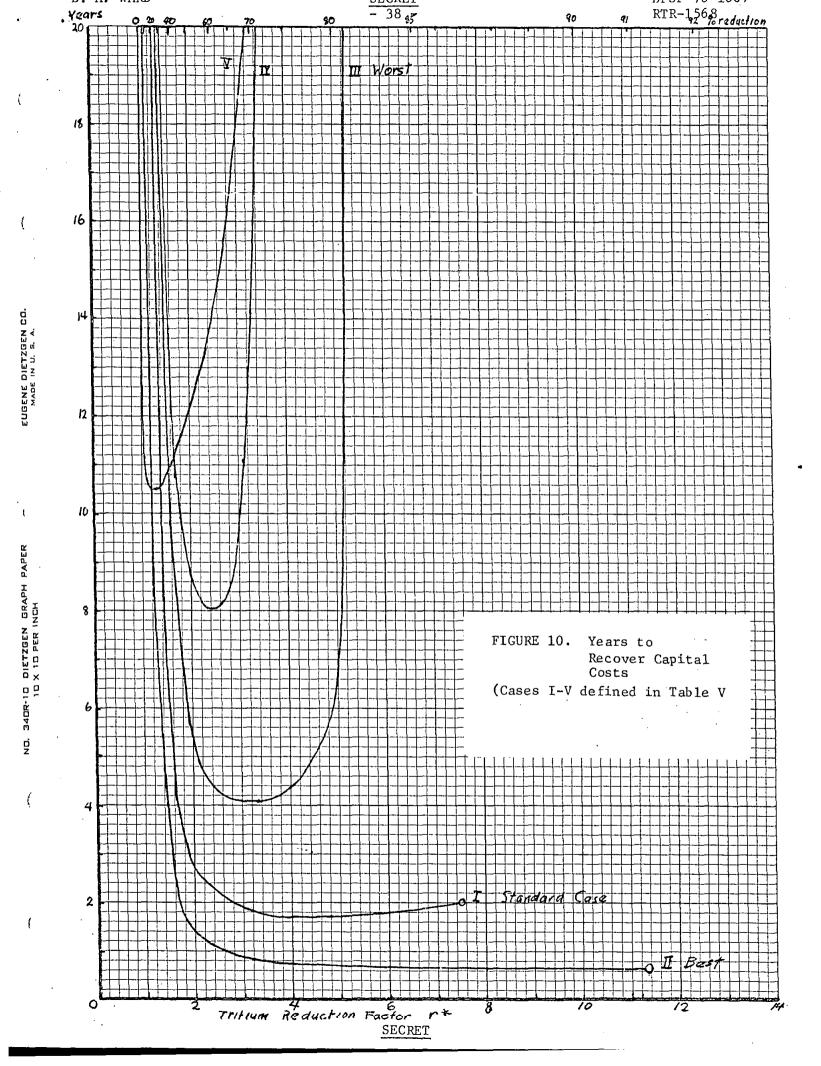


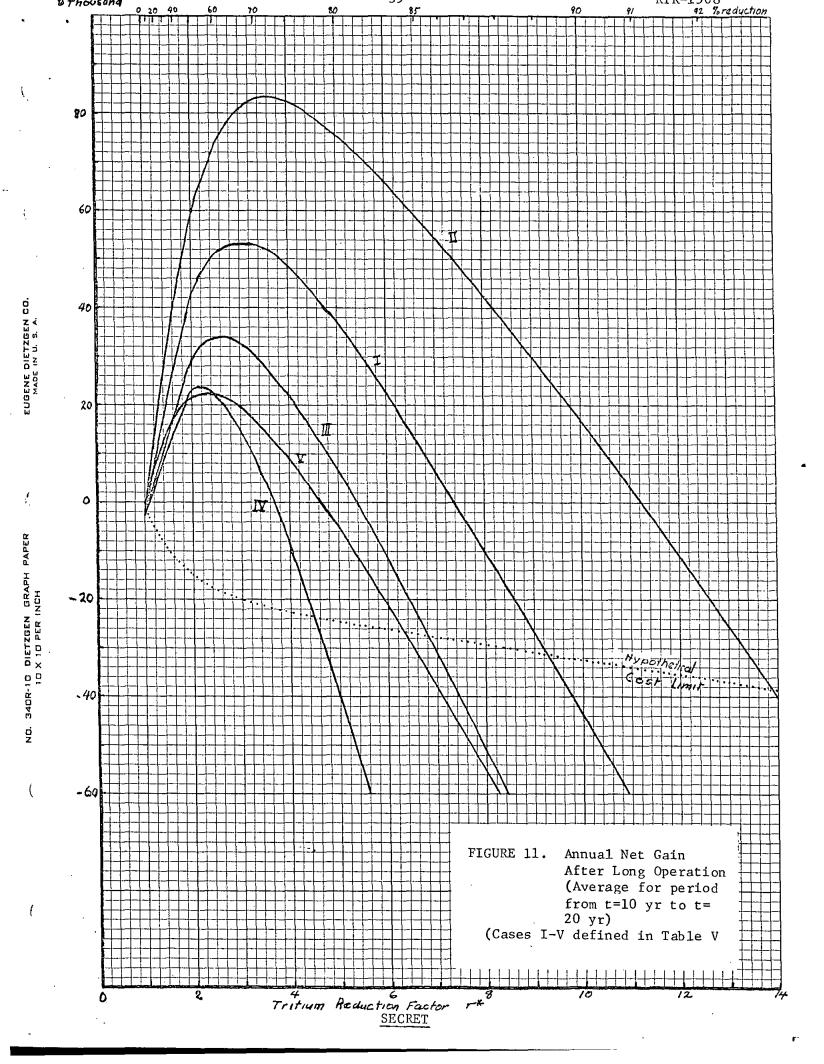
FIGURE 6. Catalytic Exchange Detritiator For A Reactor











APPENDIX A

COLUMN DESIGN EQUATIONS

In an ideal plate column, the liquid and gas stream leaving each plate are at equilibrium. The mol fraction x of tritium in the liquid and the mol fraction y of tritium in the gas leaving the same plate satisfy the equilibrium equation $x(1-y)/(1-x)y = \alpha$. At the very low tritium concentrations which will be encountered in removal of tritium from the reactor tank, this reduces to $x = \alpha y$, which we will call the assumption of linear equilibrium. Note that in this treatment we have ignored the effect of the reaction 2DTO = $D_2O + T_2O$ which becomes important only at much higher tritium concentrations.

A tritium balance of each plate and of the whole plate column, with plates satisfying this equilibrium condition, then produces the equation

$$x_b - x_t = (x_{t-1} - x_t)(\beta^n - 1)/(\beta - 1)$$
 (7)

where
$$\beta = R\alpha$$
 (8)

In equation 7, x_t is the tritium concentration in the liquid stream entering the top plate, x_{t-1}^t is that in the liquid stream leaving the top plate to flow down onto the next lower plate, and x_b is the tritium concentration in the liquid stream leaving the bottom plate.

We claim no credit for the tritium separation effected by the electrolytic cell at the bottom of the column, which is actually equivalent to somewhat more than one throretical plate of the catalyst column. Thus we assume that the isotopic composition of the gas and product streams leaving the electrolytic cell are identical and equal to that of the liquid stream entering this cell (see figure 6). When we combine this assumption with the preceding material balance and equilibrium considerations, we obtain the following column design equation:

$$n = log [1 + S(\beta - 1)/m(\alpha - 1)]log\beta$$
 (9)

The detailed derivation of this equation is given in reference 7, p 10-19. The notation used is that of reference 13.

Equation 6 (figure 1) and equation 8 are used to obtain the value of β for operation of a column that will give a desired overall separation S (e.g. the value S = 35 chosen for the cost studies). Equation 9 is then used to determine the number of theoretical plates needed. The design parameter m is adjusted by trial to obtain the optimum design. Extensive trials showed that a near optimum design for the catalytic exchange process can be obtained with a value of m \leq 0.1. The reflux ratio obtained from equation 6 with values of m in this range are so nearly 1 that the feed rate F cannot differ significantly from the gas flow rate G given by equation 5.

It has been shown (reference 10 and also reference 7, p 13) that the equivalent theoretical plate assumption is valid for packed columns if the correct value of the H.E.T.P. is used. This value is

$$H.E.T.P. = \frac{\ln \beta}{\beta - 1} \qquad \frac{L}{Ka}$$
 (10)

where K is the overall mass transfer coefficient for transfer across the liquid - gas interface and a is the interfacial area per unit height of packed column. This equation should be valid for catalytic liquid-gas exchange because research done at the Chalk River Laboratory has shown that the rate of exchange is controlled by transfer across the liquid gas interface. The catalyst is so effective in speeding up the chemical steps of the exchange reaction that these steps have negligible influence compared to the slower diffusion through the film.

The above equation shows that the H.E.T.P. depends on the separation factor $_{\alpha}$ of the particular hydrogen isotopes being separated (because β = R α and R \approx 1). In our calculations we assumed the same H.E.T.P. for the HTO-D $_2$ O separation as for the HDO-H $_2$ O separation. Equation 10 gives an H.E.T.P. for HTO-D $_2$ O that is half that for HDO-H $_2$ O, with a resulting cost of catalyst and column half what we used.

APPENDIX B

SOURCES AND UNCERTAINTIES OF DESIGN AND COST DATA

The sources and uncertainties of data listed in tables I, II, and IV are discussed in this appendix succinctly and serially in the order in which they appear in the tables. For easy cross reference, they are numbered here as in the tables. Values accurate to 1% or better are simply designated "accurate".

Table I Reactor Parameters

- 1. A mean value of V accurate to within 5%
- Average moderator loss rate for 1974. Current rate for 1975 is about 810 lb/mo. Data from K. E. Kehr. Density taken as 1.107 gm/ml = 9.24 lbs/gal. L accurate to ± 20%.
- 3. Tritium half life = 12.26 years; λ = (ln 2)/half life. Accurate
- 4. Λ_0 calculated from 1, 2 and 3. Accuracy \pm 6%.
- 5. Coefficient calculated from 1 and 4. Accurate to 8%.

Table II Dollar Benefit Data and Equations

- A. Release to Environment.
 - 1. One third of calculated off-plant exposure within 50 mile radius attributable to 100 Area tritium releases during 1974 (data furnished by W. R. Jacobsen). Presumed accurate.
 - 2. If moderator tritium concentration and D_2O loss rate remain unchanged, the exposure over a period of t years would be 29.8 t. The additional terms allow for the reduction in releases because of detritiation.

B. Basin Purging

- 1. E. C. Bertsche estimates 180 to 240 deionizer regenerations per year attributable to basin purging.
- 2. T. M. Rial estimates 200 Area charge for deionizer regeneration at \$1000 per deionizer, and a labor cost for disconnecting, transporting and hooking up again of \$200 to \$400.
- 3. $70 \times $1300 = $91,000 + 20\%$

C. Plastic Suit Work

- 1. Total number of suits used in 3 areas in 1971 through 1974 = 15600; average per reactor year = 1300
- 2. Cost of plastic suits

\$7.20/suit

Cost of added working time (30 minutes avg./suit at \$10.00/hr)

\$5.00/suit

Total added cost

\$12.20/suit

- 3. 1300 x \$12.20 = \$15,860 accurate to within a factor of two
- D. Value of Tritium
 - 1. Reference 1. Accurate to +2%.
 - 2. L. C. Brown gives \$2615; the quantity of tritium is too small to affect the scheduling of other production to meet the demand. In addition there is a potential market as fuel for fusion reactors at a considerably higher price (perhaps \$5,000/gm). Use \$2440 as a conservative figure which will give a round number for the total value which follows
 - 3. 410 x \$2440 = \$1,000,000 \pm 12%

Table IV Cost Data

1. Equation \$83 (gpy) $^{0.6}$ fits manufacturer's forecast price for electrolytic cells not yet in production: -

Cell size (gph)	.038	5	20	200
Date available	·Now	Jan. 1976	Jul. 1976	1977
Forecast price	\$3000	\$50,000	\$100,000	\$500,000
Forecast price \$83 (gpy)	\$2772	\$51,797	\$112,000	\$473,870

Thus $$83 \text{ (gpy)}^{0.4}$ estimates cost/gpy accurate to within perhaps 20%.

2. Electrical auxiliaries Basis: reference 14

For an electrolytic system of 1.53×10^4 kw capacity, rectifiers, switch gear and instrumentation were estimated to cost \$3.5 x 10^6 , or \$228.60 per kw in 1965. Cost of electricity in 1975 (\$0.022/kwh) shows a factor of 3 inflation compared to the \$0.007/kwh quoted in reference 2. Assuming the same inflation factor for equipment costs, this gives \$686.40/kw in 1975.

The electrolytic cells to be used consume 20.9 kwh per gallon of D_2O electrolyzed; 1 gph = 8760 gpy. This gives a cost/gpy of \$1.64/gpy for electrical auxiliaries. Accurate perhaps to a factor of 2.

- 3. Column hardware (includes the column shell, pumps, piping, gas recombiners, etc.) Basis: pure guess. Reference 14 gives a cost of such hardware for a purely electrolytic process as 2/3 the cost of electrolytic cells. The cell cost in item 1 above is about \$1.00/gpy.

 Assume about twice this cost, or \$2.00/gpy. Accuracy uncertain; perhaps to factor of 2.
- 4. D20 inventory Basis: negligible holdup in cells and column. Operate 1 month on reactor feed and then process all product to return D20 to reactor service. Inventory is then one month's production. This results in \$0.452/gpy for inventory value at \$50.00/lb. Actual value will depend on an economic balance between cost of D20 inventory and cost of processing product at any particular frequency.
- 5. $\underline{200 \text{ Area capital costs}}$ \$30,000 to \$35,000 for uranium bed to dehydrate the T_2 D_2 gas mixture received from the 100 Area detritiation process (reference 11). \$35,000 used in present calculations and treated as accurate.
- 6. Other capital cost pure guess.
- 7. Electricity Power at \$0.022/kwh (Power Department).

 Power demand = 20.9 kwh/gal (cell characteristic, based on manufacturer's specifications). Accurate to +20%. Gives (20.9)(\$0.022) = \$0.460/gal to within 20%.
- 8. Catalyst Current price = \$1000/cu.ft. (presumed accurate) Volume required = 7.8×10^{-6} cu.ft./gpy/plate (assumed same as Table III value for H_2O-D_2O) uncertain by factor of two. No. of plates = $20 \text{ (}\pm50\%\text{; probably on high side)}$.
 - Catalyst life = .5 (arbitrary; uncertain by factor of 2 or more). Listed Unit cost = $$1000 \times 7.8 \times 10^{-6} \times 20/0.5 = $0.31/gpy/year$, uncertain by a factor of roughly 4. Two conservatisms absorb some of the uncertainty: the separative effect of the electrolytic cells has not been included, and 2 plates is twice the number needed based on the column performance data used in this report.
- 9. Cooling Water Basis: J. C. Bixell (Mound Laboratory) estimate of cooling water requirements for T_2O-H_2O separation by catalytic exchange, scaled down in proportion to electrical power requirements (reference 15). Accuracy: to factor of two.

- 10. <u>Labor</u> Basis: J. C. Bixell estimate of direct labor plus supervision plus payroll burden, scaled down in proportion to electrical power requirements (reference 15). Accuracy: to factor of two.
- 11. Maintenance 4% of capital cost. Accuracy: ±30%
- 12. 200 Area Process Annual Costs Flat \$2,000 per month labor charge independent of quantity processed. Assumed accurate at present (reference 11).
- 13. Other 10% of capital cost. Accuracy: unknown.

REFERENCES

- 1. Towler, O. A., "Detritiation of Reactor Moderator", RTR-1562, DPSP-75-1170, June 13, 1975.
- 2. Longtin, F. B., "Trip Report: AECL Chalk River Laboratories", RTR-1564, July 3, 1975.
- 3. Lin, K. H., report, "Tritium Enrichment by Isotope Separation Technique", ORNL-TM-3976, December 1972.
- 4. Works Technical Department Monthly Progress Reports (all Secret):
 - a. DPSP-65-1-11, p 142, November 1965
 - b. DPSP-70-1-8, p 27, August 1970
 - c. DPSP-71-1-12, p 22, December 1971
 - d. DPSP-72-1-4, p 24, April 1972
 - e. DPSP-72-1-5, p 33, May 1972
 - f. DPSP-73-1-11, p 24, November 1973
 - g. DPSP-75-1-6, pR32, June 1975
- 5. McIntyre, H. C., "Natural-Uranium Heavy-Water Reactors", Scientific American, 233 No 4 p 17-27, October 1975.
- 6. Stevens, W. H., and Blackstein, F. P., "Heavy Water Production Using Hydrogen Water Exchange" in AECL Research and Development in Engineering, Winter 1973 (Atomic Energy of Canada, Ltd., AECL-4606 (Winter 1973).
- 7. Longtin, F. B., Notebook, DPSPN 818, p 1-4, 10 et seq., July 1975.
- 8. Trevorrow, L. E. and Gibson, M., "Storage and Disposal of Tritium: Evaluation of Tritium Concentration by Hydrogen Water Exchange" in Chemical Engineering Division Waste Management Quarterly Report, ANL 8152, July September 1974.
- 9. Longtin, F. B., "Detritiation of Reactor Moderator", RTR-1452, DPSP-73-1539, November 29, 1973 (Secret).
- 10. Perry, J. H., Editor, "Chemical Engineers' Handbook", 3rd Ed., p 549-550, McGraw Hill Book Co, Inc., N. Y., N. Y. 1950.
- 11. Jacober, W. J. and Ward, D. E., "Recovery of Tritium from 100 Area Moderator", DPSP-75-1241, October 6, 1975 (Secret).
- 12. Federal Register, Vol. 40, No 87-Monday, May 5, 1975, p 19442.
- 13. Randall, M. and Longtin, F. B., "Separation Processes", Ind. Eng. Chem. 30, 1063-7, 1188-92, 1311-15 (1930); 31 908-11, 1295-9 (1931).

- 14. Proctor, J. F., Report, "Preliminary Design and Cost Study of a Plant for the Concentration of Tritium . . .", DP-959, June 1965 (Secret).
- 15. Bixell, J. C., (Monsanto Corporation, Mound Laboratories), "Catalytic Detritiation of Nuclear Waste Water", oral presentation, Sept. 30, 1975.